Chapter 5

Energy-Conversion Properties of Substrate-Attached vs. Freestanding Polymer-Supported Si Wire Array Photoelectrodes

5.1 Introduction

While current silicon solar cells require ultrahigh purity silicon, device physics modeling shows that silicon wires with radial junctions can achieve high energy-conversion efficiencies using lower purity material that has a low ratio of its minority-carrier collection length to its optical absorption depth.^{33, 34} To date, however, device efficiencies for radial junction Si photovoltaics fabricated using potentially inexpensive techniques, such as the vapor-liquid-solid (VLS) growth process,⁴² have been low. Single-wire Si cells grown this way have demonstrated efficiencies up to 3.4% with a low open-circuit voltage (V_{oc}) of 260 mV,¹³⁷ while modeling on a Si wire predicts efficiencies over 17% and $V_{oc} \sim 600$ mV based on measured diffusion lengths.³⁴ Several groups have also studied solar cells using an array of Si wires.¹³⁸⁻¹⁴² Top-down approaches such as etching wire arrays from a high-quality, single-crystal wafer have produced efficiencies

around 0.5% and V_{oc} of 290 mV,¹³⁹ while the more economically relevant scenario of using bottom-up VLS-grown Si wire arrays has so far been limited to efficiencies of ~ 0.1% and $V_{oc} < 390$ mV.^{141, 142} These reports, while promising, leave much room for improvement.

The best Si wire arrays, those with the most controllable and uniform dimensions and best vertical alignment, have used single-crystal growth substrates.^{106, 119, 143} Because VLS-grown Si wires proceed in the <111> direction,⁴² using a Si(111) substrate promotes vertical orientation of the array. However, the benefit of using a wire array is undermined unless there is a way of reusing the expensive Si substrate. We have developed a technique to transfer the wire array into a film of polydimethylsiloxane (PDMS), a low-cost, transparent, flexible polymer, with both ends of the wires exposed for contacts,¹⁴⁴ and a scheme to recycle the growth substrate repeatedly so that it is a minor expense in the overall fabrication process (see Chapter 4).¹⁴⁵ Proving that these flexible, inorganic Si wire/polymer composite films can function as efficient photoelectrodes is an important step towards the production of a scalable, affordable wire array solar cell.

The VLS-grown Si wire array electrodes in liquid-junction photoelectrochemical cells reported herein yielded higher external quantum efficiencies and open-circuit voltages than previously reported wire array cells.¹³⁸⁻¹⁴² Substrate-free, polymer-supported Si wire array photoelectrodes exhibited current-potential behavior similar to that of the wires epitaxially attached to the growth substrate. Furthermore, the quantum efficiency of the wire arrays as a function of wavelength and angle of incidence indicated that the devices

produced more photocurrent than expected based solely on their geometric packing fraction.

5.2 Si Wire Array Photoelectrodes

5.2.1 Wire Array Properties

Figures 5.1a and 5.1b show representative scanning electron microscope (SEM) images of substrate-attached and peeled, polymer-supported Si wire arrays, respectively. The wires were grown by the vapor-liquid-solid (VLS) method from a Cu catalyst that was deposited in lithographically defined holes in a Si oxide buffer layer on the surface of a Si growth substrate.¹¹⁹ Cu was chosen instead of the more commonly used Au as the growth catalyst, due to the higher abundance of Cu in the Earth's crust as well as the less deleterious effect of Cu as an impurity in p-Si based solar cells.⁹⁷ An etch was used to remove the Cu catalyst tips from the wires prior to their use as photoelectrodes (see Section 5.2.2). Consistently, $> 10 \ \mu m$ minority-carrier collection lengths have been measured on individual Si microwires grown by this method.^{34, 121} The $\sim 1.5 \ \mu m$ radius of the Si microwires should thus enable efficient radial minority-carrier collection while the 100 µm length of the wires is comparable to the necessary planar thickness for efficient absorption of incident photons with energies greater than the 1.1 eV indirect band gap of Si. The wire arrays were partially embedded in polydimethylsiloxane (PDMS) and peeled off the growth substrate, yielding a flexible, processible material that consisted of ordered arrays of crystalline Si wires with their bases embedded in, but most of their length projecting out from, the PDMS film (Figures 5.1b and 5.1c). An ohmic contact to the wires was made by evaporating ~ 300 nm of Au onto the back side of the PDMS film. Although the polymer/wire composite films were subsequently attached to a Ti foil to facilitate their use as photoelectrodes, replacement of this foil with a bendable current collector would yield a fully flexible device. Current-voltage measurements using a microprobe station on the polymer-supported cells showed that essentially all of the wires were contacted using this method (see Section 5.2.3). The photoelectrochemical energy-conversion properties of these polymer-supported wire arrays were then compared to those of a photoactive, planar crystalline Si bulk electrode as well as an array of nominally identical VLS-grown Si wires that were produced on, and still physically attached to, a photoinactive, p^+ -Si substrate.



Figure 5.1. Si wire array photoelectrodes. Cross-sectional view SEM images of (a) a substrate-attached wire array (with the Cu catalyst tips still present) and (b) a peeled, polymer-supported wire array. The PDMS layer in (b) was deliberately made thicker than was typically used, to facilitate SEM imaging of the structure. The scale bar for (a,b) is 50 μ m. (c) SEM image of a peeled, polymer-supported wire array demonstrating the flexibility of these films. Scale bar for (c) is 200 μ m.

5.2.2 Electrode Fabrication and Processing

The Si wire array growth process has been described in detail elsewhere (see Section 3.5.3).¹¹⁹ In this work, 300 nm of thermally evaporated Cu (99.9999%, ESPI) was used as the catalyst in all growths. The substrates were < 0.001 Ω -cm p⁺-Si(111) wafers that were coated with a 300 nm thick thermal oxide (Silicon Quest International). The gas flow composition during wire growth was 500 sccm H₂, 10 sccm SiCl₄, 1 sccm dopant (0.25% BCl₃ in H₂) at 1 atm total pressure. The wire growth was allowed to proceed for 30 min, so that the wires were ~ 1.5 – 1.7 µm in diameter and 90 ± 15 µm long, with little length variation within a particular sample. The wires were formed on the substrate in a square arrangement having a 7 µm pitch. Following growth at 1000 °C, the reactor tube was purged with N₂(g), and over the course of ~ 30 min was allowed to cool to ~ 750 °C before the sample was removed. A doping concentration in the wires of 10¹⁷ cm⁻³ was determined by a series of lithographically defined 4-point probe measurements on individual wires.¹²¹ A LEO 1550 VP field-emission SEM at a 20 keV accelerating voltage was used to characterize the arrays.

Prior to being made into an electrode, each Si sample was etched for 10 s in 10% aq. HF, 10 min in 6: 1: 1 H₂O: 30% H₂O₂: concentrated HCl (v/v) at 70 °C (RCA2 clean), 10 s in 10% aq. HF, and then 2 min in 20% aq. KOH. The samples were thoroughly rinsed in 18 M Ω -cm resistivity H₂O and dried with N₂(g) between each step. This process removed the Cu catalyst tip and the top surface layer of the wires, but left the thermal oxide on the growth substrate intact.

The wire arrays were embedded in polymer and stripped from the underlying wafer using a procedure that closely followed our published methods (see Section 4.2).¹⁴⁴ In this process, 4.4 g of hexamethylcyclotrisiloxane (HMCTS, 98%, Alfa Aesar) was dissolved in ~ 5 mL methylene chloride, then mixed with 1.1 g of Sylgard 184 polydimethylsiloxane (Dow Corning, 1.0 g PDMS base, 0.1 g PDMS curing agent). This mixture was spin-coated onto the wire arrays at 1000 rpm for 1 min, then heated at 150 °C for 30 min. The HMCTS boiled off at this temperature without cross-linking into the PDMS, allowing the polymer to contract below the tips of the wires and cure conformally at the bases of the wires. This procedure produced a 10 – 20 µm thick layer of PDMS at the bottoms of the Si wires. The polymer-supported wire arrays were then mechanically removed from the underlying Si substrate using a razor blade.

Planar Si photoelectrodes were made from 1–2 Ω -cm p-Si(111) wafers. Ohmic back contacts were made to the substrate-attached wire array and to the planar electrodes by rubbing a Ga/In eutectic mixture onto the back side of the Si wafer. To make back contacts to the polymer-supported films, the polymer samples were carefully unrolled, taped down to a glass slide, and then ~ 300 nm Au was thermally evaporated onto the film. The polymer/wire films were then carefully painted onto squares of Ti foil using conductive silver paint to facilitate their use as photoelectrodes. Both types of wire arrays were silver-painted to a coiled Cu wire. The wire was placed in a glass tube and the electrode edges were sealed in Hysol 9460 epoxy.

Immediately prior to use in the photoelectrochemical cell, the polymer-supported electrodes were subjected to an oxygen plasma to remove any residual PDMS adhered to

the exposed Si wires and to convert the PDMS surface from hydrophobic to hydrophilic so that the aqueous liquid electrolyte could effectively penetrate the array. For each electrode, the plasma generator (March PX-500) was run for 180 s at 600 W with 330 mTorr O_2 . Before photoelectrochemical measurements, all of the electrodes were etched in 10% aq. HF for 10 s to remove the surface oxide.

5.2.3 Microprobe Station Measurements

To investigate the effectiveness of the back contact to the polymer-supported wire arrays, a Signatone H100 Series Probe Station was used to make contact to the tops of Si wires and, in combination with a Keithley 237 Source-Measure Unit, bias them to -1 V and measure the resulting current. A total of 50 points were measured on 4 different samples for substrate-attached wire arrays along with another 50 points on 4 different samples for peeled, polymer-supported wire arrays. At -1 V, the average current measured was 0.11 \pm 0.05 mA for the substrate-attached samples and 0.08 \pm 0.04 mA for the freestanding, polymer-supported samples. The error in the measurements was due to the variation in the number of wires contacted each time, which was difficult to control on such a fine scale using this probe station. However, all probed points gave a reasonable current, demonstrating that there were no large dead areas on the peeled array films.

5.3 Photoelectrochemistry

5.3.1 Methyl Viologen Electrolyte

The use of a liquid-junction photoelectrochemical cell (Figure 5.2) allowed for the evaluation of the energy-conversion performance of the wire arrays without the challenges associated with producing high-quality radial solid-state junctions, transparent conductors, or metallic grid emitter contacts. Although published Si wire array photoelectrochemical cells to date have demonstrated low efficiencies (around 0.1%),^{141,} ¹⁴² we have recently shown that with controlled p-type doping by the in situ addition of BCl₃ during the array growth, Cu-catalyzed p-Si wire arrays attached to the Si substrate in contact with aqueous methyl viologen electrolyte yield drastically improved performance.¹⁴⁶ The aqueous solution containing methyl viologen (MV^{2+}/MV^{+}) as the redox species permeated the full length of the wire array to form a highly rectifying, conformal contact with p-type Si,^{147, 148} yielding a high barrier height, along with opencircuit voltages (V_{oc}) > 550 mV and near the bulk diffusion/recombination limit on planar, crystalline Si samples under illumination conditions that produced short-circuit photocurrent densities (J_{sc}) of 25 mA cm⁻². The MV⁺ radical cation is highly absorbing across much of the visible (350 - 750 nm) spectrum,¹⁴⁹ which gives the test electrolyte an intense, violet color. To minimize confounding effects due to solution absorbance, 808 nm laser light was used to excite the Si photoelectrodes in all of the comparisons reported herein. A calibrated photodiode was placed in the solution at the height of the wire array electrode to monitor the in situ illumination intensity.

5.3.2 Photoelectrochemical Cell Setup

For electrochemical measurements, a flat-bottomed glass cell was filled with 50 mL of aqueous 0.05 M methyl viologen dichloride (MV^{2+} , Aldrich 98%), 0.5 M K₂SO₄, and buffered at pH = 2.9 using 0.1 M potassium hydrogen phthalate and sulfuric acid. The cell was constantly purged with H₂O-saturated Ar. The cell contained a standard calomel reference electrode (SCE), a Pt mesh counter electrode separated from the main compartment by a medium porosity glass frit, a large carbon cloth electrode, a small carbon cloth electrode, a face-down Si working electrode (wire array or planar), and a calibrated Si photodiode (Thorlabs) that was carefully positioned at the same height as the Si working electrode surface (Figure 5.2). To minimize mass-transport limitations, a stir bar was placed next to the Si electrode and stirred as vigorously as possible without causing vortexing, by using a magnet attached to an electric motor (NWSL 12270-9) that was controlled by a DC power supply (Rail Power 1370).

Both the oxidized and reduced form of the redox couple must be present for a cell to have a well-defined potential. As mixed, only the MV^{2+} form was present in any appreciable quantity, so the solution was electrolyzed before each measurement to produce the MV^+ radical species. The solution was electrolyzed to -0.6 V vs. SCE using the large carbon cloth as working electrode, the Pt mesh as counter electrode, and the SCE as reference. This process produced ~ 3 mM MV⁺ and turned the solution a dark violet color ($E^{o'}(MV^{2+/+}) = -0.67$ V vs. SCE). The solution potential was monitored and adjusted periodically to maintain a value of -0.6 V vs. SCE. Current-potential data were obtained using the Si as the working electrode, the large carbon cloth as the counter electrode, and the small carbon cloth (poised at the solution potential) as the reference. A 1 W, 808 nm diode laser (Thorlabs L808P1WJ) was used to minimize the solution absorbance. The power output of the laser was adjustable, and the calibrated photodiode was used to determine the light intensity incident on the Si working electrode. A Princeton Applied Research model 273 potentiostat was used to collect the currentpotential data.



Figure 5.2. Diagram of the cell setup used for photoelectrochemical measurements. Monochromatic 808 nm illumination was used to minimize solution absorbance. A calibrated photodiode was kept in solution at the height of the Si working electrode to monitor the in situ illumination intensity (image credit: S.W. Boettcher).

5.4 Photoelectrochemical Energy-Conversion Properties

5.4.1 External Quantum Efficiency vs. Potential Behavior

Figures 5.3, 5.4, and 5.5 compare the current density vs. potential (*J*-*E*) behavior of a planar p-Si wafer, a substrate-attached wire array, and a peeled, polymer-supported Si wire array, respectively. The *J*-*E* data at various light intensities have been displayed on a common graph by presenting the data in terms of the measured external quantum efficiency, which is directly proportional to the observed photocurrent density.

When using a monochromatic illumination source, it is more meaningful to describe the current in terms of the quantum efficiency. A given photon will have an energy dependent upon its wavelength. However, a photon above the band gap can only excite one electron to the conduction band of a semiconductor to be collected as current (in the absence of multi-exciton generation), with the additional energy being wasted as heat as the electron thermalizes to the conduction band energy. Therefore, different wavelengths of light with the same input illumination intensity will result in different currents in a solar cell. The external quantum efficiency (Φ_{ext}) is the fraction of photons incident on the solar cell that produce a charge-carrier collected as current. The equation to convert current to Φ_{ext} is then:

$$\Phi_{\text{ext}} = \frac{\text{electrons}}{\text{incident photon}} = \frac{i\frac{1}{q}}{P\frac{\lambda}{hc}} = \frac{i \times 1240 \frac{\text{mW nm}}{\text{mA}}}{P \times 808 \text{ nm}}$$
(5.1)

where *i* is the current in mA, *q* is the electronic charge, *P* is the power incident on the cell in mW, λ is the wavelength in nm (808 nm in this work), *h* is Planck's constant, and *c* is the speed of light.

5.4.2 Planar Electrodes

As shown in Figure 5.3, at light intensities $\leq 40 \text{ mW cm}^{-2}$, the planar p-Si photoelectrode exhibited $\Phi_{\text{ext}} \sim 0.7$, in accord with the value expected for specularly reflective, highquality bulk Si samples.¹⁵⁰ The decline in the short-circuit external quantum yield ($\Phi_{\text{ext,sc}}$) at higher light intensities resulted from mass-transport effects in the solution, while the increase in open-circuit voltage with illumination intensity occurred because the value of V_{oc} depends logarithmically on the photocurrent. The high Φ_{ext} , along with $V_{oc} \sim 530 -$ 570 mV, demonstrated that the methyl viologen liquid electrolyte effectively formed a high barrier-height junction with the p-Si surface.



Figure 5.3. Effect of intensity on planar photoelectrode performance. Plot of external quantum efficiency (Φ_{ext}) vs. potential (*E*) for different illumination intensities using a planar photoelectrode. Inset shows semilogarithmic (lin-log) plots of J_{sc} and V_{oc} vs. intensity.

5.4.3 Wire Array Electrodes

Figures 5.4 and 5.5 depict the *J-E* behavior of substrate-attached and freestanding polymer-supported wire array photoelectrodes, respectively. The photoelectrochemical response observed from the substrate-attached wire arrays arose primarily from the Si wires, because as established previously, the presence of the thermal oxide, combined with the use of degenerately doped p-Si substrates, minimized the photoelectrochemical response from the Si substrate.¹⁴⁶ The *J-E* behavior of the polymer-supported wire arrays

was very similar to that of the wire array on the growth substrate (Table 5.1, Figures 5.4, 5.5, and 5.6). The most noticeable difference was in the fill factor, which improved after casting the PDMS into the Si wires (even if the array was not then peeled from the substrate), consistent with the presence of shunts through the base of the substrate-attached wire arrays. However, the fill factor of photoelectrodes made from substrate-attached wire arrays that were not embedded in PDMS (Figure 5.4) improved significantly when a surface etch was performed immediately prior to measurement of the *J-E* behavior,¹⁴⁶ suggesting that a Cu-rich surface layer might still be present on the wires despite the use of a Cu etch prior to electrode fabrication. However, this etch caused irreversible damage to the polymer-supported electrodes (see Section 5.5.2), precluding a direct comparison of the array performance under these more optimal conditions.

The $\Phi_{\text{ext,sc}}$ values observed for the polymer-supported wire array photoelectrodes were slightly lower than those observed for the substrate-attached wire arrays without PDMS (Table 5.1, Figure 5.6). This difference is expected because the PDMS covered the bottom 10 – 20 µm of the Si wires, preventing those regions from directly exchanging current with the electrolyte. The observed $\Phi_{\text{ext,sc}} = 0.2 - 0.3$ is significant, especially considering that the packing fraction (percentage of the cross-sectional device area occupied by wires) of the array was ~ 4%. Without enhanced photon capture, a 4% packing fraction would result in a $\Phi_{\text{ext,sc}}$ of ≤ 0.04 .

The $V_{\rm oc}$ values measured for wire array photoelectrodes, although ~ 150 mV lower than the planar electrode, are higher than those previously measured on Si nanowire arrays.^{137, 139-142} The decrease in $V_{\rm oc}$ is attributed to an increase in dark current from the increased junction area of the wire array relative to the planar electrode, as well as from the increased effects of surface recombination (see Section 2.5.3).¹⁵¹ A decrease in wire size from the ~ 1.5 μ m radius investigated herein would thus result in a lower V_{oc} without a concomitant increase in J_{sc} , in accord with the lower photovoltages observed for photoelectrodes formed using Si nanowires.^{137, 139, 140}



Figure 5.4. Effect of intensity on substrate-attached wire array photoelectrode performance. Plot of external quantum efficiency (Φ_{ext}) vs. potential (*E*) for different illumination intensities using a substrate-attached wire array without PDMS. Inset shows semilogarithmic (lin-log) plots of J_{sc} and V_{oc} vs. intensity.



Figure 5.5. Effect of intensity on peeled, polymer-supported wire array photoelectrode performance. Plot of external quantum efficiency (Φ_{ext}) vs. potential (*E*) for different illumination intensities using a peeled, polymer-supported wire array without PDMS. Inset shows semilogarithmic (lin-log) plots of J_{sc} and V_{oc} vs. intensity.

	Substrate-attached			
Intensity (mW cm ⁻²)	20	40	60	80
$\Phi_{\mathrm{ext,sc}}$	0.36 ± 0.06	0.29 ± 0.05	0.25 ± 0.05	0.22 ± 0.04
J_{sc} (mA cm ⁻²)	4.6 ± 0.7	7.4 ± 1.3	9.8 ± 1.8	11.6 ± 2.1
$V_{oc}({ m mV})$	356 ± 21	398 ± 16	422 ± 16	437 ± 17
FF	0.26 ± 0.03	0.27 ± 0.02	0.27 ± 0.03	0.28 ± 0.03
$\eta_{808} \left(\%\right)^{b}$	2.2 ± 0.6	2.0 ± 0.6	1.9 ± 0.5	1.8 ± 0.5
η _{808,corr} (%) ^c	3.1 ± 0.8	3.0 ± 0.8	2.8 ± 0.8	2.7 ± 0.8
	Peeled, polymer-supported			
Intensity (mW cm ⁻²)	20	40	60	80
$\Phi_{\mathrm{ext,sc}}$	0.27 ± 0.04	0.23 ± 0.04	0.20 ± 0.03	0.18 ± 0.03
J_{sc} (mA cm ⁻²)	3.5 ± 0.5	6.0 ± 0.9	7.9 ± 1.3	9.6 ± 1.6
$V_{oc}(\mathrm{mV})$	339 ± 29	373 ± 29	390 ± 30	402 ± 31
FF	0.36 ± 0.05	0.36 ± 0.04	0.35 ± 0.05	0.35 ± 0.04
$\eta_{808}(\%)^{ m b}$	2.1 ± 0.3	2.0 ± 0.3	1.8 ± 0.2	1.6 ± 0.2
$\eta_{808,corr}$ (%) ^c	2.8 ± 0.4	2.8 ± 0.4	2.6 ± 0.4	2.4 ± 0.4

Table 5.1. Wire array photoelectrochemical cell performance data.^a

^aAverages and standard errors were calculated using 10 different samples of both substrate-attached and peeled, polymer-supported wire arrays.

^bThis efficiency is for monochromatic 808 nm illumination.

^cThis efficiency is for monochromatic 808 nm illumination after correcting for concentration overpotential and uncompensated resistance losses.



Figure 5.6. Effect of PDMS layer on photoelectrochemical behavior. Plot comparing the external quantum efficiency (Φ_{ext}) vs. potential (*E*) behavior of a substrate-attached wire array without PDMS, a substrate-attached wire array with PDMS cast on it, and a peeled, polymer-supported wire array electrode under 60 mW cm⁻² of 808 nm illumination. Dashed lines are the photoelectrode behavior corrected for concentration overpotential and solution resistance losses. All three electrodes came from the same Si wire array sample.

5.4.4 Corrections for Concentration Overpotential and Uncompensated Series Resistance

Assessing the inherent energy-conversion behavior of the wire array electrodes requires correction for any concentration overpotential and uncompensated resistance losses that arise from the use of this unoptimized test electrolyte. The corrected Φ_{ext} vs. *E* behavior (Figure 5.6, dashed lines) reveals the performance of the photoelectrodes that would be obtained in a thin-layer cell that had minimal concentration overpotential and solution resistance losses, with the corrected efficiency values for each type of wire array photoelectrode summarized in Table 5.1. The concentration overpotential is the voltage that is necessary to create a concentration gradient and drive the charge-transferring redox species in solution to the electrode surface. The solution resistance refers to the ohmic series resistance of the liquid electrolyte. Equations have been derived to account for these losses.^{152, 153} The overpotential depends on the limiting anodic and cathodic currents, which depend on the concentrations of the two forms of the redox couple. The equation for correcting the potential is:

$$E_{corr} = E - iR_{cell} - \eta_{conc} \tag{5.2}$$

$$\eta_{conc} = \left(\frac{k_B T}{nq}\right) \left\{ \ln\left(\frac{J_{l,a}}{-J_{l,c}}\right) - \ln\left(\frac{J_{l,a} - J}{J - J_{l,c}}\right) \right\}$$
(5.3)

Where E_{corr} is the corrected potential, E is the measured potential, i is the measured current, R_{cell} is the cell solution resistance, η_{conc} is the concentration overpotential, J is the current density, and $J_{l,a}$ and $J_{l,c}$ are the mass-transport-limited anodic and cathodic current

densities. $J_{l,a}$ and $J_{l,c}$ were estimated from the limiting current measured for the specific electrode of interest in forward bias and from measurements made on a glassy carbon electrode in the same cell configuration, respectively. The uncompensated cell solution resistance, $R_{cell} \sim 20 \Omega$, was extracted from the inverse slope of the *J-E* curve collected using the glassy carbon working electrode, after correction for the concentration overpotential using Equation 5.3.

5.5 Effect of Cu Impurities

5.5.1 Planar Electrodes

The effect of the Cu catalyst used for wire growth on the electronic properties of the arrays is of significant interest in this work. Based on the VLS growth mechanism,⁴² it is expected that the Si wires produced will be saturated with the catalyst metal to the solubility limit at the growth temperature. However, it has been shown that the high diffusivity of Cu in p-Si at room temperature allows most of the metal to out-diffuse to the surface and/or defect sites, suggesting that the bulk concentration most likely approaches the room temperature solubility limit.¹⁵⁴ To investigate the effect of this Cu saturation, we annealed planar Si samples of the same doping as the wires with Cu metal and compared them to pure planar electrodes.

Planar photoelectrodes used $1 - 2 \Omega$ -cm p-Si(111) wafers (Silicon Quest International). To prepare Cu-saturated samples, the wafers were etched for 2 min in 10% aq. HF immediately prior to having a 300 nm Cu layer (99.9999%, ESPI) thermally evaporated onto the front surface. They were then annealed at 1000 °C under 500 sccm H_2 at atmospheric pressure for 30 min in the same reactor used to grow Si wire arrays. The reactor tube was purged with N_2 and allowed to cool to ~ 750 °C over the course of ~ 30 min before the sample was removed. Cu annealed wafers underwent the same etch treatment as the wire arrays before being made into electrodes. Back contact was made to both types of planar samples using Ga/In eutectic. Both types of planar electrodes were tested in the same aqueous methyl viologen electrolyte used to measure wire array photoelectrodes.

Figure 5.7 shows the resulting photoelectrochemical behavior at 60 mW cm⁻². The pure, unannealed planar Si exhibited good solar cell properties, as shown in Figure 5.3. After being annealed with Cu, however, the fill factor of the Φ_{ext} curve dropped from 0.47 to 0.28, which is close to that observed for substrate-attached Si wire arrays (Table 5.1). We speculate that a Cu-rich surface layer causes this loss. Even though the Si surface was etched with 20% aq. KOH before being made into an electrode, more Cu could out-diffuse to the surface in the time between the etch and the photoelectrochemical measurement (a day or more). After conducting a 2 min etch in 20% aq. KOH at room temperature immediately before the measurement, the fill factor improved back to 0.49. Excepting some loss in V_{oc} , the KOH-etched, Cu-annealed planar electrode behavior was nearly as good as the pure planar Si, indicating that the level of Cu present does not affect the bulk Si electronic properties too adversely.



Figure 5.7. Effect of Cu impurities on planar photoelectrodes. Plot of the external quantum efficiency (Φ_{ext}) vs. potential (*E*) of planar p-Si before and after annealing in the presence of Cu. Annealed performance is shown with and without a KOH surface etch immediately prior to the measurement. Illumination intensity was 60 mW cm⁻² at 808 nm.

5.5.2 Wire Array Electrodes

As with Cu-annealed planar electrodes, the fill factor of substrate-attached wire arrays was observed to improve markedly with a $1 - 2 \min 20\%$ aq. KOH etch immediately before taking measurements (Figure 5.8). Again we propose that this enhancement is due to the removal of a Cu-rich surface layer from the wires. The optimized substrate-attached Si wire array performance has been reported elsewhere.¹⁴⁶ Unfortunately, this surface etch proved deleterious to polymer-supported wire array electrodes, making a direct comparison with this method impractical (Figure 5.8a). Although it is not entirely

clear what effect the KOH had on these electrodes, we believe damage was occurring to the back contacts. The same behavior for both types of electrodes was observed even if the initial KOH etch prior to electrode fabrication was allowed to run longer. While it would have been ideal to conduct the surface etch before applying the polymer, the need to cast PDMS, peel the film, evaporate a metallic back contact, and prepare the surface with a plasma etch to produce a polymer-supported wire array electrode took too long for the benefit of the KOH etch to be noticeable. When measured one day after a KOH etch, the substrate-attached wire array electrode returned to its reduced fill factor state, demonstrating that the benefit of this surface treatment is temporary (Figure 5.8b). Cu is known to preferentially diffuse to p^+ over p-Si areas,¹⁵⁴ indicating that the Cu concentration in the growth substrate should be significantly higher than the wires. The diffusion of additional Cu from the substrate to the wires after the KOH surface etch could account for the energy-conversion properties reverting back to their pre-etch behavior. Future improvement of the peeled, polymer-supported wire array energyconversion properties could therefore be pursued by a new surface etch that does not damage the delicate electrode or by thoroughly gettering Cu impurities out of the wires and growth substrate before applying PDMS (i.e., leaving the substrate-attached arrays in FeCl₃ for an extended period of time to siphon out Cu).



Figure 5.8. Effect of KOH etch on wire arrays. (a) Plot of the external quantum efficiency (Φ_{ext}) vs. potential (*E*) for substrate-attached and peeled, polymer-supported wire array electrodes with and without a KOH surface etch immediately prior to the measurement. Both of these electrodes came from the same Si wire array. (b) Plot of the external quantum efficiency (Φ_{ext}) vs. potential (*E*) for a different substrate-attached wire array electrode before a KOH surface etch, immediately after the KOH etch, and one day after the KOH etch. Illumination intensity was 60 mW cm⁻² at 808 nm.

5.6 Spectral Response

5.6.1 Substrate-Attached vs. Peeled, Polymer-Supported Wire Arrays

The spectral response properties of the wire array photoelectrodes were evaluated in aqueous methyl viologen as a function of the angle of incidence (Figure 5.9).¹²² The $\Phi_{ext,se}$ values observed at 808 nm were in good agreement with those measured at low light intensity using the 808 nm laser. As observed previously, the quantum efficiency of the wire array photoelectrode was highly dependent on the angle of incidence.^{122, 146} At angles significantly off normal, the optical path length through the substrate-attached wires increased, less light passed completely in the regions between wires, and $\Phi_{ext,sc} >$ 0.6 (Figure 5.9a). The peeled, polymer-supported wire array spectral response also showed an increase in $\Phi_{ext,sc}$ at higher angles, with a maximum of $\Phi_{ext,sc} \sim 0.45$ (Figure 5.9b).

The angular dependence of $\Phi_{ext,sc}$ suggests that more disorder was present in the peeled wire array electrodes than in the substrate-attached array electrodes, resulting in additional scattering that reduced the dependence of $\Phi_{ext,sc}$ on the angle of incidence. SEM images of the substrate-attached wires showed a well-defined array with a uniform wire geometry (Figure 5.10a). Such structures also produced a distinct, square optical diffraction image when illuminated with a 633 nm He-Ne laser beam (Figure 5.10b). Embedding the wires in PDMS (and leaving the wires on the substrate) made the diffraction pattern less distinct (Figure 5.10d), even though the SEM image still showed an ordered structure (Figure 5.10c), presumably because the polymer surface induced some optical scattering. Peeling the polymer-supported array and silver-painting it to a metal foil to make an electrode (see Section 5.2.2), produced distinct domains in the surface of the array, as revealed by SEM images (Figure 5.10e), and the loss of the ordered optical diffraction pattern (Figure 5.10f). The enhanced scattering due to this disorder is consistent with the reduced dependence of $\Phi_{ext,sc}$ on the incidence angle for the peeled, polymer-supported wire arrays.



Figure 5.9. Si wire array spectral response. 2-dimensional color maps depicting the short-circuit quantum yield, $\Phi_{ext,sc}$ at low intensity as a function of wavelength and angle of incidence for (a) a substrate-attached wire array without PDMS and (b) a peeled, polymer-supported wire array.



Figure 5.10. Increased scattering in peeled, polymer-supported wire array electrodes. (a,c,e) Top-down SEM images of (a) a substrate-attached wire array, (c) a substrate-attached wire array with PDMS cast on the base, and (e) a peeled, polymer-supported wire array silver-painted to a Ti substrate in the manner used to prepare photoelectrodes. The silver-painting process produced clearly distinguishable contours in the thin film. The scale bar for (a,c,e) is 50 μ m. (b,d,f) Diffraction patterns resulting from the reflection of a 633 nm He-Ne laser off of (b) a substrate-attached wire array, (d) a substrate-attached wire array with PDMS cast on the base, and (f) a peeled, polymer-supported wire array silver-painted to a Ti substrate. While the periodic, square arrangement of the wires is clearly evident in the diffraction pattern of (b), the scattering introduced by the PDMS layer made the pattern less crisp in (d), and the loss of strict periodicity in (e) caused enough disorder that no discernible pattern was evident in (f).

5.6.2 Spectral Response and Diffraction Image Setup

The apparatus used for spectral response measurements has been described in detail elsewhere.¹²² The same aqueous methyl viologen electrolyte was used, with stirring, as for photoelectrochemical measurements. A glass box cell with an open top was used, to allow for the rotation of the working electrode. Using a Pt coil counter electrode and a Ag/AgCl reference electrode, the photoresponse of the wire arrays were measured at -400 mV vs. the reference, with the bias chosen to position the photoelectrochemical cell near short-circuit conditions based on the cell's observed current-potential behavior. Absolute V_{oc} values were not necessary and hence optically transparent electrolyte solutions were used ($[MV^{2+}]/[MV^{+}] > 1$), allowing measurements across the full visible spectrum. A custom-built, motorized stage enabled computerized control of the illumination incidence angle by adjusting the position of the working electrode. Normal incidence was set by directing the laser approximately perpendicular to the wire array surface and then minimizing the photoresponse. A tunable, collimated light source was achieved by coupling a supercontinuum laser (Fianium) to a monochromator along with a chopper and lock-in amplifier. Data were collected in 2 nm increments. $\Phi_{ext,sc}$ was determined by relating the photoresponse of the wire arrays to a calibrated photodiode that had been placed in nominally the same location within the cell.

To produce diffraction images, a 633 nm He-Ne laser source of spot size $\sim 1 \text{ mm}^2$ was passed through a small hole in a vertical plate to strike the wire array electrodes at approximately normal incidence. The resulting diffraction pattern was reflected back

onto the vertical plate. Images were taken in the absence of room light, using a digital camera mounted on a tripod.

5.7 Conclusion

The behavior of the peeled, polymer-supported Si wire film relative to the unpeeled, substrate-attached wire array electrode demonstrates that Si wires can be transferred into inexpensive, flexible films without sacrificing their solar energy-conversion performance. The single-wavelength Φ_{ext} and V_{oc} values reported herein are large compared to those reported for previous Si nanowire array solar cells, and the spectral response data showed high $\Phi_{ext,sc}$ across the entire visible spectrum. The peeled wire/polymer composite photoelectrode had $\Phi_{\text{ext,sc}}$ values that ranged from 0.28 (approximately 7 times the packing fraction, $\sim 4\%$) at normal incidence to 0.45 at high angles of incidence ($\sim 50^{\circ}$). By increasing the packing fraction and exploring designs that lengthen the path of light through the wires, quantum efficiencies approaching that of planar bulk Si should be attainable from the peeled wire array photoelectrodes. If optical absorption by the redox species can be minimized, improving the J_{sc} to 35 mA cm⁻² indicates that energyconversion efficiencies > 5% are possible under AM 1.5 illumination even without improving the other uncorrected characteristics of these polymer-supported wire array photoelectrodes.¹⁵⁵ The overpotential-corrected data demonstrate that better performance is achievable in optimized liquid-junction or solid-state cell configurations. The results indicate that a flexible, Si wire array solar cell with a competitive efficiency is possible based on wire array architectures without the need for a supporting crystalline Si wafer.